

PATENT ABSTRACTS OF JAPAN

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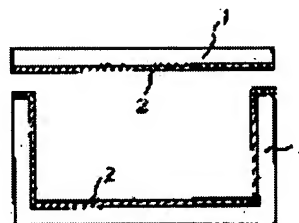
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(54) PRODUCTION OF POLYURETHANE MOLDED PRODUCT

(57)Abstract:

PURPOSE: To economically produce a urethane molded product without being accompanied by the deterioration of working environment or working efficiency by using a mold whose cavity surface is coated with a ceramic layer and introducing a gas or liquid containing water and/or alcohol into the mold at the time of mold release to demold a molded product.

CONSTITUTION: In a method for producing a polyurethane molded product by molding a polyurethane molding raw material using a mold, the cavity surface of a mold main body 1 is coated with a ceramic layer 2 and a gas or liquid containing water and/or alcohol is introduced into the mold at the time of mold release to demold the molded product. By introducing the gas or liquid containing water and/or alcohol into the mold, said gas or the liquid penetrates in the gap between the mold and the molded product to function as a release material and demolding becomes easy and the molded product can be easily released without applying a release agent to the mold.



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CLAIMS

[Claim(s)]

[Claim 1] The manufacture approach of the polyurethane mold goods characterized by unmolding mold goods after introducing in a mold the gas or liquid with which a cavity side contains water and/or alcohol using the mold covered with the ceramic layer in the manufacture approach of the polyurethane mold goods which fabricate a polyurethane shaping raw material using a mold at the time of mold release.

[Claim 2] The approach according to claim 1 of performing by blowing this gas into a mold for installation of the gas containing water and/or alcohol, or putting a mold into the ambient atmosphere of this gas.

[Claim 3] The approach according to claim 1 of performing by pressing this liquid fit for installation of the liquid containing water and/or alcohol in a mold, or immersing a mold into this liquid.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] the manufacture approach of polyurethane mold goods that this invention contains urethane RIM (reaction injection molding) mold goods, such as polyurethane foaming articles, such as a seat cushion, and an urethane bumper, -- it is especially related with the manufacture approach of the polyurethane mold goods which can be released from mold easily.

[0002]

[Description of the Prior Art] Polyurethane (it is hereafter written as urethane) is general-purpose resin which shows a broad property and is used for various applications. When generation of the urethane polymer by the reaction of polyol and the poly isocyanate is a base and manufacture of urethane considers as foam, along with this reaction, physical or chemical foaming is performed to coincidence. After urethane mold goods prepolymer-ize the unreacted shaping raw material (one-shot process) or the main raw material which blended various additives with the polyol and the poly isocyanate which are the main raw material, they are manufactured from the shaping raw material (the prepolymer method) which blended the additive in many cases. That is, foaming is performed to coincidence by a polymerization reaction, shaping, and the need.

[0003] The assembled die which has a predetermined cavity is used for the seat cushion of an automobile, and it pours in thru/or injects the above-mentioned shaping raw material in a mold, if it is required within a mold, it will be heated, produces a polymerization and foaming, and is usually manufactured by unmolding so that it may be one of the greatest applications of urethane foam mold goods and may be called a molded product.

[0004] As a mold used for this approach, the mold made of thermosetting resin, such as metal molds, such as aluminum and iron, or an epoxy resin, and polyester resin, is used. However, reactivity is very high, since this activity reaction is performed within a mold, it is easy to paste up a Plastic solid on a mold, and a mold-release characteristic is bad [the generation reaction of the urethane polymer mentioned above]. Therefore, release agents, such as a silicone system and a wax system, are applied to a cavity side so much for every molding cycle, and the fabrication operation is usually carried out.

[0005] However, use of a lot of release agents has produced various kinds of faults in shaping of urethane foam. For example, a product is polluted by work environment, a mold, and the pan by the release agent. Moreover, in order to remove the release agent which fixed in the mold, it is necessary to wash with a solvent the release agent which fixed for every fixed molding cycle. In order for work environment to get worse further and to interrupt an activity by dealing with an volatile solvent for use of a lot of release agents and solvents to be not only lost economically, but, working efficiency also falls.

[0006] Although to perform coatings of non-adhesiveness, such as a fluororesin, to the cavity side of a mold was also tried in order to avoid use of a release agent, fluororesin coating tends to separate the top whose effectiveness is not enough, and there is a trouble that the endurance of a mold falls and it is not put in practical use.

[0007] A ceramic sintered compact is formed in the cavity side of a mold at JP,63-144211,U, and sinking in and the good die of the mold-release characteristic which carried out printing are indicated by this ceramic sintered compact in the fluororesin. Although improved about endurance, this mold has in addition inadequate mold-release characteristic, when using it for shaping of urethane polymer.

[0008]

[Problem(s) to be Solved by the Invention] The purpose of this invention is offering the manufacture approach of an urethane Plastic solid excellent in the mold-release characteristic which can unmold an urethane Plastic solid easily, without using a release agent and fluororesin covering. Another purpose of this invention is offering the approach an urethane Plastic solid's being manufactured economically, without being accompanied by aggravation of work environment or working efficiency.

[0009]

[Means for Solving the Problem] this invention persons made the coating layer of a ceramic exist in the cavity side of a mold, as a result of advancing research aiming at achievement of the above-mentioned purpose, and when the gas or liquid which contains water and/or alcohol before unmolding was introduced, they acquired the unexpected knowledge that a Plastic solid could be unmolded easily. This invention is completed based on this knowledge.

[0010] Here, in the manufacture approach of the polyurethane mold goods which use a mold and fabricate a RIURETAN shaping raw material, using the mold by which the cavity side is covered in the ceramic layer, after the summary of this invention introduces in a mold the gas or liquid which contains water and/or alcohol at the time of mold release, it is in the manufacture approach of the urethane mold goods characterized by unmolding mold goods.

[0011]

[Function] Hereafter, the configuration of this invention is explained with the operation. Especially the class of urethane mold goods manufactured by the approach of this invention is not limited. That is, the approach of this invention is applicable to elasticity, half-hard and hard urethane foam, thermosetting and thermoplastic urethane elastomer, and a pan at manufacture of the Plastic solid of the urethane resin of arbitration, such as denaturation urethane, such as urethane urea and urethane acrylate. What is necessary is just to choose as usual the urethane raw material which the urethane shaping raw material used for manufacture of each of these urethane products is common knowledge at this contractor, therefore is used for the approach of this invention according to the product made into the purpose. Generally an urethane shaping raw material is reactant mixture which uses as the main raw material the poly isocyanate which reacted unreacted or imperfectly, and polyol.

[0012] When manufacture of urethane foam mold goods is taken for an example, an urethane shaping raw material is the poly isocyanate and polyol. (or prepolymer to which both this component was made to react) A catalyst, foaming size modifier s (an example, silicone resin, emulsifier, etc.) Foaming agent (an example, water, Freon, a methylene chloride, a pentane, or air introduced by machine churning) It is the mixture to contain.

[0013] Especially the mold used for shaping of an urethane shaping raw material is the cavity side, although not limited. (namely, field in contact with an urethane raw material) What is covered with the ceramic layer is used. Although the class or the manufacture approach of a mold are not limited as long as the cavity side is covered with the ceramic layer, generally it is desirable to use an assembled die.

[0014] Formation of a ceramic layer can be formed by spreading and printing containing the same technique as ceramic coating, i.e., one sort, and two sorts or more of ceramic raw material compounds (compound which forms a ceramic by printing) of aqueous coating liquid.

[0015] As for the ceramic layer covered in a mold, it is desirable that it is that to which a front face has compatibility in water and/or alcohol at least. Since it is thought that many things which have water and alcoholic compatibility are in a ceramic, the ceramic layer of a mold may be formed by the ceramic-coating method better known than before.

[0016] The desirable formation approach of a ceramic layer applies the liquefied constituent containing one sort or two sorts or more of ceramic raw material compounds (such a compound may be hereafter called a compatibility ceramic raw material compound) with water and/or alcohol, and the radical of

compatibility to the cavity side of a mold, and consists of carrying out printing (namely, comparatively low temperature and/or a short time) of the spreading layer under the conditions on which water and/or alcohol, and the radical of compatibility remain partially at least.

[0017] As water and/or a ceramic raw material compound of alcoholic compatibility, it is [metals (in this invention, semimetals, such as silicon and boron are also included in a metal), such as aluminum, Cr, Mg, Si, Ti, calcium, Sr and Ba and] water (H_2O). There is a compound containing a component. Water (H_2O) A component is heavy water to the ion which constitutes H_2O , such as the H_2O itself and H^+ , OH^- , H, and OH, or a non-ion part, and a list. (D_2O) And the same ion as the above-mentioned or a non-ion part is meant. Moreover, the metallic compounds containing the same component of alcohol can also be used. The compatibility over water and/or alcohol is given to a compound by such component.

[0018] As an example of such a compatibility ceramic raw material compound, there is an all complex of the above-mentioned metal, i.e., the metal complex formed of an olation reaction. For this, between metal atoms is two or more $OH(s)$. - It is a complex with the structure of cross linkage over which the bridge was constructed by the radical or H_2O . By adding a hydrochloric acid to the water solution of a sodium silicate, and carrying out pH adjustment, an all complex can form the hydrosol of a silicic acid and can form it by gelling this by request.

[0019] Another desirable compatibility ceramic raw material compound of a class is the alkoxide complex of metals, such as Si, Ti, and aluminum. A metal alkoxide complex is formed by dissolving for example, a metal hydroxide in alcohol, and has the structure which the alkoxide radical configured in a metal.

[0020] There are metallic compounds containing hydrogen ions, such as acid salt of water metallic compounds, such as metal acid chloride, such as a silicic acid, antimoniac acid, a stannic acid, an ulmin acid, and a titaniac acid, silicon, antimony, tin, aluminum, and titanium, and these metals, in the example of other compatibility ceramic raw material compounds which can be used. For example, even if it uses the aquosity coating liquid containing an alkali-metal silicate, especially the coating liquid which added acids, such as an alkali and/or boric acids, such as ammonium hydroxide and an amine, and a phosphoric acid, to this, the ceramic layer which shows compatibility to water and/or alcohol can be formed.

[0021] One sort of such a compatibility ceramic raw material compound or two sorts or more form the dissolution, colloid-izing or the solution currently distributed, the colloidal solution, or slurry-like aquosity coating liquid in water, and present spreading. It is others, namely, powder, such as water and/or alcohol and the ceramic raw material compound of non-compatibility, for example, a metal nitride, (an example, silicon nitride, alumimium nitride), carbide (silicon carbide), a boride, and a silicide, can be made to live together for the viscosity control of liquid, or the other purpose in coating liquid. As other ingredients in which coating liquid is made to live together and it deals, a water-insoluble nature metal salt, for example, an alkaline earth metal carbonate, a sulfate (an example, a barium sulfate, and barium carbonate), etc. are in metaled oxide (an example, a silica, an alumina, a titanium dioxide, chrome oxide) and a list.

[0022] Although especially the loadings are not limited when making the ceramic raw material compound of non-compatibility live together in coating liquid, it is desirable that the rate of these non-compatibility compounds becomes especially 30 or less % of the weight 50 or less % of the weight to the total quantity of a ceramic raw material compound. What is necessary is for especially a limit not to have the concentration of coating liquid, either, and just to adjust so that the liquid of the suitable viscosity for spreading may be obtained. The sum density of the ceramic raw material compound in coating liquid is usually 30 or less % of the weight preferably 50 or less % of the weight.

[0023] The coating liquid which contains the ceramic raw material compound of compatibility in this water and/or alcohol is applied to the cavity side of a mold with suitable spreading means, such as a dip painting cloth, spraying spreading, and roll coating. If required, they are a suitable organic solvent or an aquosity penetrant remover about a mold before spreading. (an example, alkaline cleaning liquid) It washes, and a front face is degreased and defecated. Although metal things of a mold, such as

aluminum, iron, and various alloys, are desirable, the mold made from organic materials, such as a mold made from inorganic materials, such as gypsum, plastics, and wood, can also be used. The above-mentioned coating liquid may be applied to parts other than the cavity side of a mold by request.

[0024] Component which gives the water after spreading and in a compatibility compound, and/or compatibility with alcohol s (an example, an OH radical, H₂O, an alkoxide radical, alcohol, etc.)

Printing of low temperature and/or a short time is comparatively performed so that it may remain partially at least. Although stoving temperature changes also with ingredients which constitute the class and mold of a ceramic raw material to be used, generally, it is within the limits of 120-300 degrees C preferably, and 100-600 degrees C of printing time amount are 10 minutes - 2 hours preferably for 5 minutes to 5 hours. Printing can be carried out in air or inert gas, such as nitrogen or an argon.

[0025] In this way, as for the manufactured mold, the component of compatibility remains partially at least to water and/or alcohol in the ceramic layer in which a metal did not become an oxide but was formed completely.

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TECHNICAL FIELD

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PRIOR ART

[Description of the Prior Art] Polyurethane (it is hereafter written as urethane) is general-purpose resin which shows a broad property and is used for various applications. When generation of the urethane polymer by the reaction of polyol and the poly isocyanate is a base and manufacture of urethane considers as foam, along with this reaction, physical or chemical foaming is performed to coincidence. After urethane mold goods prepolymer-ize the unreacted shaping raw material (one-shot process) or the main raw material which blended various additives with the polyol and the poly isocyanate which are the main raw material, they are manufactured from the shaping raw material (the prepolymer method) which blended the additive in many cases. That is, foaming is performed to coincidence by a polymerization reaction, shaping, and the need.

[0003] The assembled die which has a predetermined cavity is used for the seat cushion of an automobile, and it pours in thru/or injects the above-mentioned shaping raw material in a mold, if it is required within a mold, it will be heated, produces a polymerization and foaming, and is usually manufactured by unmolding so that it may be one of the greatest applications of urethane foam mold goods and may be called a molded product.

[0004] As a mold used for this approach, the mold made of thermosetting resin, such as metal molds, such as aluminum and iron, or an epoxy resin, and polyester resin, is used. However, reactivity is very high, since this activity reaction is performed within a mold, it is easy to paste up a Plastic solid on a mold, and a mold-release characteristic is bad [the generation reaction of the urethane polymer mentioned above]. Therefore, release agents, such as a silicone system and a wax system, are applied to a cavity side so much for every molding cycle, and the fabrication operation is usually carried out.

[0005] However, use of a lot of release agents has produced various kinds of faults in shaping of urethane foam. For example, a product is polluted by work environment, a mold, and the pan by the release agent. Moreover, in order to remove the release agent which fixed in the mold, it is necessary to wash with a solvent the release agent which fixed for every fixed molding cycle. In order for work environment to get worse further and to interrupt an activity by dealing with an volatile solvent for use of a lot of release agents and solvents to to be not only lost economically, but, working efficiency also falls.

[0006] Although to perform coatings of non-adhesiveness, such as a fluororesin, to the cavity side of a mold was also tried in order to avoid use of a release agent, fluororesin coating tends to separate the top whose effectiveness is not enough, and there is a trouble that the endurance of a mold falls and it is not put in practical use.

[0007] A ceramic sintered compact is formed in the cavity side of a mold at JP,63-144211,U, and sinking in and the good die of the mold-release characteristic which carried out printing are indicated by this ceramic sintered compact in the fluororesin. Although improved about endurance, this mold has a in addition inadequate mold-release characteristic, when using it for shaping of urethane polymer.

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EFFECT OF THE INVENTION

[Effect of the Invention] As explained in full detail above, it becomes possible to release urethane mold goods from mold easily from a mold, without applying a release agent by introducing an urethane shaping raw material into a mold using the mold with which the ceramic layer was prepared in the cavity side, and introducing the content gas or liquid of water and/or alcohol in a mold before unmolding by the approach of this invention.

[0052] Thereby, in the fabrication operation of the conventional urethane mold goods, spreading to the cavity side of a lot of release agents for indispensable every molding cycle becomes unnecessary. consequently, when spreading for every complicated molding cycle of this is lost and a fabrication operation is simplified, on various kinds of troubles and concrete target accompanying release agent spreading The work environment by the release agent, a mold, and contamination according to the release agent of a product further are lost. Moreover, solvent cleaning of the mold for every fixed molding cycle for removing the release agent which fixed in the mold, Decline in the working efficiency by a fabrication operation being interrupted by the economical loss by use of a lot of release agents and solvents, aggravation of the work environment by dealing with an volatile or poisonous solvent, and washing of a mold is avoidable.

[0053] Thus, the manufacture approach of the urethane mold goods of this invention is an approach of demonstrating the advantage which was excellent when the good product of quality was able to be manufactured efficiently and was industrially carried out by low cost at the same time it improves the environment of an urethane fabrication operation.

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TECHNICAL PROBLEM

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MEANS

[Means for Solving the Problem] this invention persons made the coating layer of a ceramic exist in the cavity side of a mold, as a result of advancing research aiming at achievement of the above-mentioned purpose, and when the gas or liquid which contains water and/or alcohol before unmolding was introduced, they acquired the unexpected knowledge that a Plastic solid could be unmolded easily. This invention is completed based on this knowledge.

[0010] Here, in the manufacture approach of the polyurethane mold goods which use a mold and fabricate a RIURETAN shaping raw material, using the mold by which the cavity side is covered in the ceramic layer, after the summary of this invention introduces in a mold the gas or liquid which contains water and/or alcohol at the time of mold release, it is it in the manufacture approach of the urethane mold goods characterized by unmolding mold goods.

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OPERATION

[Function] Hereafter, the configuration of this invention is explained with the operation. Especially the class of urethane mold goods manufactured by the approach of this invention is not limited. That is, the approach of this invention is applicable to elasticity, half-hard and hard urethane foam, thermosetting and thermoplastic urethane elastomer, and a pan at manufacture of the Plastic solid of the urethane resin of arbitration, such as denaturation urethane, such as urethane urea and urethane acrylate. What is necessary is just to choose as usual the urethane raw material which the urethane shaping raw material used for manufacture of each of these urethane products is common knowledge at this contractor, therefore is used for the approach of this invention according to the product made into the purpose. Generally an urethane shaping raw material is reactant mixture which uses as the main raw material the poly isocyanate which reacted unreacted or imperfectly, and polyol.

[0012] When manufacture of urethane foam mold goods is taken for an example, an urethane shaping raw material is the poly isocyanate and polyol. (or prepolymer to which both this component was made to react) A catalyst, foaming size modifier s (an example, silicone resin, emulsifier, etc.) Foaming agent (an example, water, Freon, a methylene chloride, a pentane, or air introduced by machine churning) It is the mixture to contain.

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[0014] Formation of a ceramic layer can be formed by spreading and printing containing the same technique as ceramic coating, i.e., one sort, and two sorts or more of ceramic raw material compounds (compound which forms a ceramic by printing) of aqueous coating liquid.

[0015] As for the ceramic layer covered in a mold, it is desirable that it is that to which a front face has compatibility in water and/or alcohol at least. Since it is thought that many things which have water and alcoholic compatibility are in a ceramic, the ceramic layer of a mold may be formed by the ceramic-coating method better known than before.

[0016] The desirable formation approach of a ceramic layer applies the liquefied constituent containing one sort or two sorts or more of ceramic raw material compounds (such a compound may be hereafter called a compatibility ceramic raw material compound) with water and/or alcohol, and the radical of compatibility to the cavity side of a mold, and consists of carrying out printing (namely, comparatively low temperature and/or a short time) of the spreading layer under the conditions on which water and/or alcohol, and the radical of compatibility remain partially at least.

[0017] As water and/or a ceramic raw material compound of alcoholic compatibility, it is [metals (in this invention, semimetals, such as silicon and boron are also included in a metal), such as aluminum, Cr, Mg, Si, Ti, calcium, Sr and Ba and] water (H₂O). There is a compound containing a component. Water (H₂O) A component is heavy water to the ion which constitutes H₂O, such as the H₂O itself and H⁺, OH⁻, H, and OH, or a non-ion part, and a list. (D₂O) And the same ion as the above-mentioned or a non-ion part is meant. Moreover, the metallic compounds containing the same component of

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[0020] There are metallic compounds containing hydrogen ions, such as acid salt of water metallic compounds, such as metal acid chloride, such as a silicic acid, antimononic acid, a stannic acid, an ulmin acid, and a titanonic acid, silicon, antimony, tin, aluminum, and titanium, and these metals, in the example of other compatibility ceramic raw material compounds which can be used. For example, even if it uses the aqueous coating liquid containing an alkali-metal silicate, especially the coating liquid which added acids, such as an alkali and/or boric acids, such as ammonium hydroxide and an amine, and a phosphoric acid, to this, the ceramic layer which shows compatibility to water and/or alcohol can be formed.

[0021] One sort of such a compatibility ceramic raw material compound or two sorts or more form the dissolution, colloid-izing or the solution currently distributed, the colloidal solution, or slurry-like aqueous coating liquid in water, and present spreading. It is others, namely, powder, such as water and/or alcohol and the ceramic raw material compound of non-compatibility, for example, a metal nitride, (an example, silicon nitride, aluminum nitride), carbide (silicon carbide), a boride, and a silicide, can be made to live together for the viscosity control of liquid, or the other purpose in coating liquid. As other ingredients in which coating liquid is made to live together and it deals, a water-insoluble nature metal salt, for example, an alkaline earth metal carbonate, a sulfate (an example, a barium sulfate, and barium carbonate), etc. are in metal oxide (an example, a silica, an alumina, a titanium dioxide, chrome oxide) and a list.

[0022] Although especially the loadings are not limited when making the ceramic raw material compound of non-compatibility live together in coating liquid, it is desirable that the rate of these non-compatibility compounds becomes especially 30 or less % of the weight 50 or less % of the weight to the total quantity of a ceramic raw material compound. What is necessary is for especially a limit not to have the concentration of coating liquid, either, and just to adjust so that the liquid of the suitable viscosity for spreading may be obtained. The sum density of the ceramic raw material compound in coating liquid is usually 30 or less % of the weight preferably 50 or less % of the weight.

[0023] The coating liquid which contains the ceramic raw material compound of compatibility in this water and/or alcohol is applied to the cavity side of a mold with suitable spreading means, such as a dip painting cloth, spraying spreading, and roll coating. If required, they are a suitable organic solvent or an aqueous penetrant remover about a mold before spreading. (an example, alkaline cleaning liquid) It washes, and a front face is degreased and defecated. Although metal things of a mold, such as aluminum, iron, and various alloys, are desirable, the mold made from organic materials, such as a mold made from inorganic materials, such as gypsum, plastics, and wood, can also be used. The above-mentioned coating liquid may be applied to parts other than the cavity side of a mold by request.

[0024] Component which gives the water after spreading and in a compatibility compound, and/or compatibility with alcohol s (an example, an OH radical, H₂O, an alkoxide radical, alcohol, etc.) Printing of low temperature and/or a short time is comparatively performed so that it may remain partially at least. Although stoving temperature changes also with ingredients which constitute the class and mold of a ceramic raw material to be used, generally, it is within the limits of 120-300 degrees C preferably, and 100-600 degrees C of printing time amount are 10 minutes - 2 hours preferably for 5

minutes to 5 hours. Printing can be carried out in air or inert gas, such as nitrogen or an argon.

[0025] In this way, as for the manufactured mold, the component of compatibility remains partially at least to water and/or alcohol in the ceramic layer in which a metal did not become an oxide but was formed completely. In this way, the component of compatibility is contained to water and/or alcohol in the ceramic (metallic oxide corresponding to used metals, such as an example, an alumina, a silica, a mullite, a titania, calcia, and a magnesia) which makes a frame, and the ceramic layer a front face indicates compatibility to be to water and/or alcohol is formed in a cavity side.

[0026] The formation approach of a ceramic layer is not limited to the above-mentioned approach. As mentioned above, the ceramic layer which shows compatibility to water and/or alcohol depending on conditions may be formed also by the conventional ceramic-coating method. That is, when the mold release approach mentioned later of making the description of this invention is applied, as long as it is the ceramic layer which shows sufficient mold-release characteristic, you may be what kind of ceramic layer. although especially the thickness of a ceramic layer is not limited -- 0.1-20 micrometers -- especially -- It is desirable to be referred to as 0.5-10 micrometers. As long as it is required, spreading may be repeated and the ceramic layer of desired thickness may be formed.

[0027] An urethane shaping raw material is introduced into this mold with common use means, such as impregnation and injection, and it is made to foam within a mold at the reaction and hardening of a raw material, and a pan in the case of foam. What is necessary is just to carry out this fabrication operation like a conventional method. As long as it is required, heat tracing of the mold may be carried out during shaping, and hardening and a foaming reaction may be promoted. The Plastic solid acquired after suitable time amount progress is unmolded from a mold. Although it may be carried out after a Plastic solid hardens this unmolding completely, before hardening is completed, it unmolds the Plastic solid with which hardening usually progressed to extent which can be released from mold from the point of working efficiency, leave it further, it makes hardening complete, and is taken as a product.

[0028] This invention has the description in the mold release approach of introducing in a mold the gas or liquid which contains water and/or alcohol before this unmolding. By installation of the gas or liquid containing this water and/or alcohol, even if it does not apply a release agent to a mold beforehand, it can release from mold easily.

[0029] The example of such a gas is water, alcohol (an example, a methanol, or ethanol), or gas containing the both steam. As for the water in gas, and/or the amount of alcohol, it is desirable that a steamy partial pressure uses the gas of the air to which a steamy partial pressure contains 30% or more of steam, and others 10% or more that what is necessary is just the amount which can attain the purpose of making mold release easy especially in the case of the gas containing a steam. The gas of a steam can also be used 100%. An alcoholic steam can also be mixed and used for the gas of air and others. The examples of the liquid containing water and/or alcohol are water, alcohol, or these mixed liquor (namely, alcoholic water solution), and can use this as it is. If a price and danger are taken into consideration, it is advantageous to use the air (for an example and a steamy partial pressure to be 30% or more of steam) containing a steam.

[0030] The amount of installation of a gas or a liquid will not be restricted especially if it is sufficient amount for unmolding to become easy. 30-150 degrees C of gaseous temperature are 50-100 degrees C preferably. In the case of a liquid, 30-90 degrees C is desirable.

[0031] Installation of the gas containing this water and/or alcohol can be performed by putting a mold into the ambient atmosphere containing the entrainment of this gas or this gas into a mold. The former approach uses the mold of the perforation which prepared the hole for a mold, and the approach of blowing a gas from this hole or blowing a gas from the crack surface of an assembled die can be used for it. The latter approach can be enforced by placing a mold fixed time into a steamy gas ambient atmosphere, or making it pass. In this case, a mold can also be made into a porous thing. Moreover, installation of water and/or an alcoholic content gas can also be promoted by decompressing the inside of a mold by vacuum suction etc. Press fit of the liquid into a mold or immersion of the mold to the inside of a liquid can perform installation of water and/or an alcoholic content liquid as well as installation of said gas.

[0032] This gas or liquid trespasses upon the gap of a mold and a Plastic solid by introducing water and/or an alcoholic content gas, or a liquid into a mold. Although it is thought that this gas or liquid functions as a release agent, and unmolding becomes easy, that reason is not clear so that it may mention later. In addition, since it is effective and simple to introduce by the shape of a gas like a steam as for water and/or alcohol, it is desirable, but it is effective, even if it is liquid like water or an alcoholic water solution and introduces.

[0033] Then, a Plastic solid is unmolded. When a large quantity did not apply a release agent to the mold in the fabrication operation of the conventional urethane mold goods, mold goods adhered to the mold firmly and mold release was difficult. In spite of using the mold with which formation of mold-release characteristic coats, such as spreading of a release agent and a fluororesin, is not performed by the approach of this invention, the reason which the difficult urethane resin of mold release releases from mold easily is not clear. The water and/or alcohol in the gas introduced into the water and/or alcohol which are contained in the ceramic layer of a mold before the compound part of compatibility and unmolding, or a liquid carry out a certain operation. Although that to which association between a mold and urethane mold goods is cut, or adhesion force is reduced is conjectured It is not known until now that water and/or alcohol have such an operation, and, for the moment, the mechanism of how water and/or alcohol participate in mold release is not solved.

[0034] In addition, the constituent of water and/or alcohol, for example, an OH radical, is a polar group, for example, in polyolefine mold goods, if corona discharge treatment is carried out and polar groups, such as an OH radical, are introduced into a mold-goods front face, it is known frame processing or that the adhesive property on the front face of mold goods will increase. Therefore, the effectiveness attained by this invention that mold release becomes easy by installation of polar groups, such as an OH radical, (that is, an adhesive property is reduced) is contrary to old technical common sense, and is a completely unexpected thing.

[0035] Thus, although the reason mold release becomes easy by the approach of this invention is not certain, at present, this invention persons are guessing as follows. However, this is a guess to the last and, thereby, this invention does not receive a certain constraint.

[0036] Various kinds of resultants which have association (an example, a urethane bond, an urea bond, amide association) which has a polarity during shaping of urethane mold goods by the reaction of an isocyanate radical and active hydrogen content radicals, such as an OH radical, an amine radical, and a carboxylic-acid radical, generate. When the mold which is not covered [conventional] is used, such polar high association that exists on the surface of mold goods carries out reaction association with the active group (for example, metal molds, such as a product made from aluminum, active metal atoms, such as metal ions, such as aluminum ion, and aluminum) which exists on the surface of a mold, and it adheres to a mold firmly. That is, mold release is conjectured to become difficult in order to combine urethane mold goods with a mold focusing on such association. If the component of compatibility exists in the ceramic layer of a mold at water and/or alcohol at this time, the water in air will stick to this part that exists in the ceramic layer front face of a mold (adhesion), this moisture will disappear in response to the time of urethane shaping with isocyanate, and adhesion of a mold and the urethane Plastic solid fabricated will arise firmly. However, since the front face of a mold is a ceramic layer with high water and/or alcohol, and compatibility when the content gas or liquid of water and/or alcohol is introduced before unmolding, a ceramic layer front face takes in water and/or alcohol there. In this way, for the front face of a mold, full water and/or alcohol destroy adhesion association with urethane and a mold, and urethane and a ceramic layer separate easily.

[0037] The mold after unmolding can carry out periodic duty repeatedly as it is. In this invention, since a release agent is not used, the difficulty accompanying extensive use of the conventional release agent is avoided.

[Translation done.]

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EXAMPLE

[Example] Next, an example illustrates the effectiveness of this invention. However, this invention is not restricted to an example.

[0039] By adding a hydrochloric acid to the work sodium-silicate water solution of example 1 mold, and adjusting to pH 5-10, it is SiO₂. The colloidal solution of the silicic-acid sol in which a content 50 - 200 g/l carried out olation was obtained. To the obtained all complex content colloidal solution, the silica impalpable powder 5 with a grain size of 1 micrometer or less - 25 g/l were added, and the coating liquid for ceramic formation was prepared to it.

[0040] The above-mentioned coating liquid was applied by immersion, the applied mold was put into the electric furnace, it baked on the cavity side of the assembled die 1 (mold cavity method 300mmx300mmx 70mm) made from aluminum of the configuration shown in drawing 1 for 30 minutes at 150 degrees C, and the ceramic layer 2 with a thickness of 1-2 micrometers was formed in it.

[0041] a fabrication operation -- urethane foam mold goods were manufactured using the mold which holds the ceramic layer of water compatibility to the cavity side manufactured as mentioned above. The used urethane raw material was a 2 liquid type thing, and the presentation before mixing was as follows in weight %.

A liquid polyol 100 weight sections catalyst (33LV) 0.4 weight sections silicone system foam stabilizer 0.3 weight sections polyol system cross linking agent 1.5 weight sections foaming agent(water) 3 Weight section B liquid TDI, A liquid of ***** of a polymeric MDI, and B liquid were mixed at a rate of 100:50, and it considered as the shaping raw material.

[0042] This urethane raw material was poured into the above-mentioned mold, it was left for 2 minutes at 70 degrees C, and a reaction, hardening, and foaming were made to perform. In this condition, hardening is not completed completely. Then, after blowing the 80-degree C air containing the steam of 90% of steamy partial pressures into the cavity for 5 minutes by the 0.5m [/second] rate of flow, mold goods were unmolded immediately. The mold release at this time is very easy, adhesion of urethane resin was not seen in the cavity side of a mold, but the front face was smooth and urethane foam mold goods without a blemish were obtained.

[0043] Although repetitive implementation of the fabrication operation of urethane foam mold goods was similarly carried out 50 times using the same mold, the mold-release characteristic was held good and was able to manufacture the urethane foam mold goods of high quality efficiently.

[0044] Manufacture of a mold and a fabrication operation were carried out like the example 1 except having introduced the ethanol water solution into the mold by impregnation 5 40-degree C% before example 2 unmolding. The result was the same as that of an example 1.

[0045] The coating liquid for example 3 ceramic formation was prepared as follows. By adding a hydrochloric acid to the water solution of a sodium aluminate, and adjusting to pH 5-10, it is aluminum 2O₃. The colloidal solution in which a content 50 - 200 g/l carried out olation was obtained. The alumina impalpable powder 5 with a grain size of 1 micrometer or less - 25 g/l were added to this all complex content colloidal solution, and it was used for it as coating liquid for ceramic formation.

[0046] This coating liquid was applied to the cavity side of a mold like the example 1, printing was

performed for 30 minutes at 150 degrees C, and the cavity side manufactured the assembled die covered with the ceramic layer with a thickness of 1-2 micrometers. Although the quantum of the content of a compound with the water compatibility component in a ceramic layer cannot be carried out, it is surmised about that it will be occupied with such [40 - 50%] a compound of surface area.

[0047] When the fabrication operation of urethane foam mold goods was carried out like examples 1 and 2 using this mold, the good mold-release characteristic was able to be held like examples 1 and 2, and repetitive implementation of the shaping was able to be carried out.

[0048] Although manufacture of a mold and a fabrication operation were carried out like example of comparison 1 example 1, the entrainment of the air containing the steam before unmolding was omitted, and it unmolded immediately after neglect for 10 minutes at 80 degrees C in ordinary atmospheric air. Mold release of mold goods was impossible.

[0049] The fabrication operation was carried out like the example 1 except having used the assembled die same with having used in the example of comparison 2 example 1 made from aluminum directly, without forming a ceramic layer. After blowing before unmolding the air which contains a steam like an example 1, when it unmolded, mold release is difficult and the appearance of mold goods was presenting ingredient destruction.

[0050] Manufacture of a mold and a fabrication operation were carried out like example of comparison 3 example 1. However, the gas entrainment before unmolding was performed using the air of 5% of steamy partial pressures. Mold release is completely impossible and the appearance of mold goods was presenting ingredient destruction.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the informality sectional view of the assembled die for urethane shaping used in the example.

[Description of Notations]

1: Body of a mold 2: Ceramic layer

[Translation done.]

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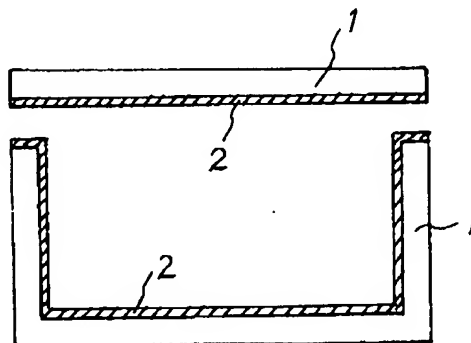
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(54) 【発明の名称】 ポリウレタン成形品の製造方法

(57) 【要約】

【構成】 型本体1のキャビティ面にセラミック層2が形成されている型に、ポリウレタン成形原料を注入または射出し、脱型前に水および/またはアルコール含有気体（水蒸気かアルコール蒸気を含有する空気など）または液体を導入する、ポリウレタンの成形方法。

【効果】 離型剤を塗布せずに容易に離型することができ、従来の多量の離型剤の使用に伴う問題点が解消される。



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【特許請求の範囲】

【請求項1】 型を用いてポリウレタン成形原料を成形するポリウレタン成形品の製造方法において、キャビティ面がセラミック層で被覆されている型を用い、離型時に水および／またはアルコールを含有する気体または液体を型内に導入してから成形品を脱型することを特徴とする、ポリウレタン成形品の製造方法。

【請求項2】 水および／またはアルコールを含む気体の導入を、該気体を型に吹込むか、または該気体の雰囲気中に型を曝すことにより行う、請求項1記載の方法。

【請求項3】 水および／またはアルコールを含む液体の導入を、該液体を型内に圧入するか、または該液体中に型を浸漬することにより行う、請求項1記載の方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、シートクッションなどのポリウレタン発泡成形品およびウレタンパンパ等のウレタンRIM（反応射出成形）成形品を含むポリウレタン成形品の製造方法、特に容易に離型可能なポリウレタン成形品の製造方法に関する。

【0002】

【従来の技術】ポリウレタン（以下、ウレタンと略記する）は、幅広い性質を示し、多様な用途に利用されている汎用樹脂である。ウレタンの製造は、ポリオールとポリイソシアネートとの反応によるウレタンポリマーの生成が基本であり、発泡体とする場合には、この反応に付随して物理的または化学的発泡が同時に行われる。ウレタン成形品は、主原料であるポリオールとポリイソシアネートに種々の添加剤を配合した未反応の成形原料（ワンショット法）あるいは主原料をプリポリマー化してから添加剤を配合した成形原料（プリポリマー法）から製造されることが多い。即ち、重合反応と成形および必要により発泡が同時に行われる。

【0003】自動車のシートクッションは、発泡ウレタン成形品の最大の用途の一つであり、型物と呼ばれるように、所定のキャビティを有する分割型を用いて上記の成形原料を型に注入ないし射出し、型内で必要であれば加熱して重合および発泡を生じさせ、脱型することにより通常は製造されている。

【0004】この方法に用いる型としては、アルミニウム、鉄などの金属製の型、あるいはエポキシ樹脂、ポリエステル樹脂などの熱硬化性樹脂製の型が使用される。しかし、前述したウレタンポリマーの生成反応は極めて反応性が高く、この活性な反応が型内で行われるため、成形体が型に接着し易く、離型性が悪い。そのため、通常は、シリコーン系、ワックス系などの離型剤を成形サイクル毎にキャビティ面に多量に塗布して成形作業を実施している。

【0005】しかし、多量の離型剤の使用は、発泡ウレタンの成形に各種の不具合を生じている。例えば、離型

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剤により作業環境、型、さらには製品が汚染される。また、型に固着した離型剤を除去するため、一定の成形サイクルごとに固着した離型剤を溶剤で洗浄することが必要となる。多量の離型剤と溶剤の使用は、経済的に損失となるだけでなく、揮発性の溶剤を取り扱うことにより作業環境はさらに悪化し、また作業を中断するため、作業効率も低下する。

【0006】離型剤の使用を避けるために、型のキャビティ面にフッ素樹脂などの非粘着性のコーティングを施すことも試みられたが、効果が十分でない上、フッ素樹脂コーティングが剥がれ易く、型の耐久性が低下するといった問題点があり、実用化されていない。

【0007】実開昭63-144211号公報には、型のキャビティ面にセラミック焼結体を形成し、このセラミック焼結体にフッ素樹脂を含浸・焼付した離型性のよい成形型が開示されている。この型は、耐久性については改善されたが、ウレタンポリマーの成形に使用する場合には離型性がなお不十分である。

【0008】

【発明が解決しようとする課題】本発明の目的は、離型剤やフッ素樹脂被覆を利用せずにウレタン成形体を容易に脱型することができる、離型性に優れたウレタン成形体の製造方法を提供することである。本発明の別の目的は、作業環境や作業効率の悪化を伴わずにウレタン成形体を経済的に製造することのできる方法を提供することである。

【0009】

【課題を解決するための手段】本発明者らは、上記目的の達成を目指して研究を進めた結果、型のキャビティ面にセラミックのコーティング層を存在させ、脱型前に水および／またはアルコールを含有する気体または液体を導入すると、成形体を容易に脱型できるという予想外の知見を得た。本発明はこの知見に基づき完成されたものである。

【0010】ここに、本発明の要旨は、型を用いてリウレタン成形原料を成形するポリウレタン成形品の製造方法において、キャビティ面がセラミック層で被覆されている型を用い、離型時に水および／またはアルコールを含有する気体または液体を型内に導入してから成形品を脱型することを特徴とする、ウレタン成形品の製造方法にある。

【0011】

【作用】以下、本発明の構成をその作用と共に説明する。本発明の方法により製造されるウレタン成形品の種類は特に限定されない。即ち、本発明の方法は、軟質、半硬質および硬質ウレタン発泡体、熱硬化性および熱可塑性ウレタンエラストマー、さらにはウレタンウレア、ウレタンアクリレートなどの変性ウレタンなどの任意のウレタン樹脂の成形体の製造に適用することができる。これらの各ウレタン製品の製造に用いるウレタン成形原

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料は当業者には周知であり、従って、本発明の方法に用いるウレタン原料は、目的とする製品に応じて従来と同様に選択すればよい。一般にウレタン成形原料は、未反応あるいは不完全に反応したポリイソシアネートとポリオールとを主原料とする反応性の混合物である。

【0012】発泡ウレタン成形品の製造を例にとると、ウレタン成形原料は、ポリイソシアネート、ポリオール（あるいはこの両成分を反応させたプリポリマー）、触媒、発泡サイズ調節剤（例、シリコーン樹脂、乳化剤など）、発泡剤（例、水、フレオン、塩化メチレン、ペンタン、あるいは機械攪拌により導入された空気）を含有する混合物である。

【0013】ウレタン成形原料の成形に使用する型は特に限定されないが、そのキャビティ面（即ち、ウレタン原料と接触する面）がセラミック層で被覆されているものを用いる。セラミック層でキャビティ面が被覆されている限り、型の種類や製造方法は限定されないが、分割型を使用することが一般に好ましい。

【0014】セラミック層の形成はセラミックコーティングと同様の手法、即ち、1種もしくは2種以上のセラミック原料化合物（焼付によってセラミックを形成する化合物）を含有する水性塗布液の塗布と焼付により形成することができる。

【0015】型に被覆するセラミック層は、少なくとも表面が水および/またはアルコールに親和性を持つものであることが好ましい。セラミックの中には水やアルコール親和性を有しているものが多くあると考えられるので、型のセラミック層は従来より公知のセラミックコーティング法により形成したものであってもよい。

【0016】好ましいセラミック層の形成方法は、水および/またはアルコールと親和性の基を持つ1種もしくは2種以上のセラミック原料化合物（以下、このような化合物を親和性セラミック原料化合物と称することがある）を含む液状組成物を型のキャビティ面に塗布し、塗布層を水および/またはアルコールと親和性の基が少なくとも部分的に残存する条件下で（即ち、比較的低温および/または短時間）焼付することからなる。

【0017】水および/またはアルコール親和性のセラミック原料化合物としては、Al、Cr、Mg、Si、Ti、Ca、Sr、Baなどの金属（本発明ではケイ素やホウ素などの半金属も金属に含める）と、水（ H_2O ）の構成部分とを含む化合物がある。水（ H_2O ）の構成部分とは、 H_2O 自体、および H^+ 、 OH^- 、 H 、 OH 等の H_2O を構成するイオンもしくは非イオン部分、並びに重水（ D_2O ）およびその前述と同様なイオンもしくは非イオン部分を意味する。また、アルコールの同様な構成部分を含む金属化合物も使用することができる。このような構成部分により、化合物に水および/またはアルコールに対する親和性が付与される。

【0018】このような親和性セラミック原料化合物の

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例としては、上記金属のオール錯体、即ち、オール化反応によって形成される金属錯体がある。これは、金属原子間が複数の OH^- 基または H_2O などで架橋された架橋構造を持つ錯体である。オール錯体は、例えば、ケイ酸ナトリウムの水溶液に塩酸を加えてpH調整をすることにより、ケイ酸のヒドロゾルを形成し、所望によりこれをゲル化することにより形成することができる。

【0019】別の種類の好ましい親和性セラミック原料化合物は、Si、Ti、Alなどの金属のアルコキシド錯体である。金属アルコキシド錯体は、例えば金属水酸化物をアルコールに溶解させることにより形成され、金属にアルコキシド基が配位した構造を持つ。

【0020】使用しうる他の親和性セラミック原料化合物の例には、ケイ酸、アンチモン酸、スズ酸、アルミン酸、チタン酸などの金属酸塩、ケイ素、アンチモン、スズ、アルミニウム、チタンなどの含水金属化合物、これら金属の酸性塩などの水素イオンを含む金属化合物がある。例えば、アルカリ金属ケイ酸塩を含有する水性塗布液、特にこれに水酸化アンモニウム、アミンなどの塩基性物質および/またはホウ酸やリン酸などの酸を加えた塗布液を用いても、水および/またはアルコールに親和性を示すセラミック層を形成することができる。

【0021】このような親和性セラミック原料化合物の1種もしくは2種以上が水に溶解、膠質化、または分散している溶液、コロイド溶液、またはスラリー状の水性塗布液を形成し、塗布に供する。塗布液には、その他の、即ち、水および/またはアルコールと非親和性のセラミック原料化合物、例えば、金属窒化物（例、窒化ケイ素、窒化アルミニウム）、炭化物（炭化ケイ素）、ホウ化物、ケイ化物などの粉末を、液の粘度調整やその他の目的で共存させることができる。塗布液に共存させる他の材料としては、金属の酸化物（例、シリカ、アルミナ、二酸化チタン、酸化クロム）、並びに水不溶性金属塩、例えば、アルカリ土類金属炭酸塩および硫酸塩（例、硫酸バリウムおよび炭酸バリウム）などがある。

【0022】塗布液に非親和性のセラミック原料化合物を共存させる場合、その配合量は特に限定されないが、セラミック原料化合物の合計量に対して、これらの非親和性化合物の割合が50重量%以下、特に30重量%以下となることが好ましい。塗布液の濃度も特に制限はなく、塗布に好適な粘度の液が得られるように調整すればよい。塗布液中のセラミック原料化合物の合計濃度は、通常は50重量%以下、好ましくは30重量%以下であろう。

【0023】かかる水および/またはアルコールに親和性のセラミック原料化合物を含む塗布液を、浸漬塗布、噴霧塗布、ロール塗布などの適当な塗布手段により型のキャビティ面に塗布する。必要であれば、塗布前に、型を適当な有機溶媒または水性洗浄液（例、アルカリ性肥皂液）で洗浄して、表面を脱脂・清浄化する。型は、ア

ルミニウム、鉄、各種合金などの金属製のものが好ましいが、石こう等の無機材料製の型、プラスチック、木材等の有機材料製の型も使用できる。所望により、上記塗布液は型のキャビティ面以外の部分に塗布してもよい。

【0024】塗布後、親和性化合物中の水および／またはアルコールとの親和性を付与する構成部分（例、OH基、 H_2O 、アルコキシ基、アルコールなど）が少なくとも部分的に残存するように、比較的低温および／または短時間の焼付を行う。焼付温度は、使用するセラミック原料の種類および型を構成する材料によっても異なるが、一般には100～600℃、好ましくは120～300℃の範囲内であり、焼付時間は5分～5時間、好ましくは10分～2時間である。焼付は空気中あるいは窒素或いはアルゴン等の不活性ガス中で実施できる。

【0025】こうして製造した型は、金属が完全には酸化物になっておらず、形成されたセラミック層中に水および／またはアルコールに対して親和性の構成部分が少なくとも部分的に残留している。こうして、骨格をなすセラミック（例、アルミナ、シリカ、ムライト、チタニア、カルシア、マグネシアなど、用いた金属に対応する金属酸化物）中に水および／またはアルコールに親和性の構成部分を含有し、表面が水および／またはアルコールに親和性を示すセラミック層がキャビティ面に形成される。

【0026】セラミック層の形成方法は上記の方法に限定されるものではない。前述したように、従来のセラミック・コーティング法でも、条件によっては水および／またはアルコールに親和性を示すセラミック層が形成される場合がある。即ち、後述する、本発明の特徴をなす離型方法を適用した場合に十分な離型性を示すセラミック層である限り、どのようなセラミック層であってもよい。セラミック層の厚みは特に限定されないが、0.1～20μm、特に0.5～10μmとすることが好ましい。必要であれば、塗布作業を反復して、所望の厚みのセラミック層を形成してもよい。

【0027】この型に、ウレタン成形原料を注入、射出などの慣用手段により導入して、原料の反応・硬化、さらには発泡体の場合には発泡を型内で行わせる。この成形作業は、常法と同様に実施すればよい。必要であれば、成形中に型を外部加熱して、硬化や発泡反応を促進させてもよい。適当な時間経過後に、得られた成形体を型から脱型する。この脱型は、成形体が完全に硬化してから実施してもよいが、通常は作業効率の点から、離型可能な程度まで硬化が進んだ成形体を、硬化が完了する前に脱型し、さらに放置して硬化を完了させ、製品とする。

【0028】本発明は、この脱型前に水および／またはアルコールを含有する気体または液体を型内に導入するという離型方法に特徴がある。この水および／またはアルコールを含有する気体または液体の導入により、型に

予め離型剤を塗布しておかなくても、容易に離型することができる。

【0029】このような気体の例は、水、アルコール（例、メタノールまたはエタノール）、或いはその両者の蒸気を含むガスである。ガス中の水および／またはアルコールの量は、離型を容易にするという目的を達成できる量であればよく、水蒸気を含有する気体の場合には、蒸気分圧が10%以上、特に蒸気分圧が30%以上の水蒸気を含有する空気その他の気体を使用することが好ましい。100%水蒸気の気体も使用できる。アルコール蒸気も、空気その他の気体に混合して用いることができる。水および／またはアルコールを含有する液体の例は水、アルコールもしくはこれらの混合液（即ち、アルコール水溶液）であり、これをそのまま用いることができる。価格および危険性を考慮すると、水蒸気を含有する空気（例、蒸気分圧が30%以上の水蒸気）を用いることが有利である。

【0030】気体または液体の導入量は、脱型が容易となるのに十分な量であれば特に制限されない。気体の温度は30～150℃、好ましくは50～100℃である。液体の場合は30～90℃が好ましい。

【0031】この水および／またはアルコールを含有する気体の導入は、型内への該気体の吹き込み、または該気体を含有する雰囲気中に型を曝すことにより行うことができる。前者の方法は、例えば、型に孔を設けた有孔の型を使用し、この孔から気体を吹き込むか、あるいは分割型の剖面より気体を吹き込む方法が採用できる。後者の方法は、蒸気ガス雰囲気中に型を一定時間置くか、あるいは通過させることにより実施することができる。この場合、型は多孔性のものとすることもできる。また、型内を真空引き等により減圧することにより、水および／またはアルコール含有気体の導入を促進することもできる。水および／またはアルコール含有液体の導入も、前記気体の導入と同様に、型内への液体の圧入、或いは液体中への型の浸漬等によって行うことができる。

【0032】型に水および／またはアルコール含有気体または液体を導入することによって型と成形体との間にこの気体または液体が侵入する。この気体または液体が離型剤として機能し、脱型が容易となるものと考えられるが、後述するように、その理由は明らかではない。なお、水および／またはアルコールは、水蒸気のように気体状で導入することが効果的かつ簡便であるため好ましいが、水またはアルコール水溶液のように液体状で導入しても効果はある。

【0033】その後、成形体を脱型する。従来のウレタン成形品の成形作業では、型に離型剤を多量の塗布しておかないと、成形品が型に強固に付着し、離型は困難であった。本発明の方法により、離型剤の塗布やフッ素樹脂などの離型性被膜の形成が行われていない型を使用するにもかかわらず、離型の困難なウレタン樹脂が容易に

離型する理由は明らかではない。型のセラミック層中に含まれる水および／またはアルコールに親和性の化合物部分と脱型前に導入した気体または液体中の水および／またはアルコールが何らかの作用をして、型とウレタン成形品との間の結合を切断するか、あるいは付着力を低下させるものと推測されるが、水および／またはアルコールにこのような作用があることはこれまで知られておらず、水および／またはアルコールが離型にいかに関与するかのメカニズムは今のところ解明されていない。

【0034】なお、水および／またはアルコールの構成成分、例えばOH基は極性基であり、例えばポリオレフィン成形品をフレーム処理またはコロナ放電処理し、成形品表面にOH基等の極性基を導入すると成形品表面の接着性が高まることが知られている。従って、OH基等極性基の導入により離型が容易となる（即ち、接着性を低下させる）という本発明により達成される効果は、これまでの技術常識には反しており、全く予想外のことである。

【0035】このように、本発明の方法により離型が容易となる理由は定かではないが、現時点では本発明者らは次のように推量している。ただし、これはあくまで推量であって、本発明はこれにより何らかの拘束を受けるものではない。

【0036】ウレタン成形品の成形中には、イソシアネート基とOH基、アミン基、カルボン酸基などの活性水素含有基との反応により、極性を有する結合（例、ウレタン結合、尿素結合、アミド結合）を持つ各種の反応生成物が生成する。従来の未被覆の型を使用した場合、成形品の表面に存在するこのような極性の高い結合が、型の表面に存在する活性基（例えば、アルミニウム製の金属製の型では、アルミニウムイオン等の金属イオン、アルミニウム等の活性金属原子）と反応結合して型に強固に付着する。即ち、ウレタン成形品は、このような結合を中心にして型と結合するため、離型が困難になると推測される。この時、型のセラミック層に水および／またはアルコールに親和性の構成部分が存在すると、型のセラミック層表面に存在するこの部分に空気中の水が吸着（付着）し、この水分がウレタン成形時にイソシアネートと反応して消滅して、型と成形されるウレタン成形体の付着が強固に生ずる。しかし、そこへ、脱型前に水および／またはアルコールの含有気体または液体を導入すると、型の表面が水および／またはアルコールと親和性が高いセラミック層であるため、セラミック層表面が水および／またはアルコールをとり込む。こうして型の表面にとりこまれた水および／またはアルコールが、ウレタンと型との付着結合を破壊し、ウレタンとセラミック層が容易に剥がれる。

【0037】脱型した後の型は、そのまま何回も反復使用できる。本発明では、離型剤を使用しないので、従来の離型剤の大量使用に伴う難点が回避される。

【0038】

【実施例】次に実施例により本発明の効果を例証する。ただし、本発明は実施例に制限されるものではない。

【0039】実施例1

型の制作

ケイ酸ナトリウム水溶液に塩酸を加えてpH5～10に調整することにより、SiO₂含有量50～200g/lのオール化したケイ酸ゾルのコロイド溶液を得た。得られたオール錯体含有コロイド溶液に、粒度1μm以下のシリカ微粉末5～25g/lを添加し、セラミック形成用塗布液を調製した。

【0040】図1に示す形状のアルミニウム製分割型1（キャビティ寸法300mm×300mm×70mm）のキャビティ面に、上記の塗布液を浸漬により塗布し、塗布した型を電気炉に入れて150℃で30分間焼付けて、厚さ1～2μmのセラミック層2を形成した。

【0041】成形作業

上記のように製作した、キャビティ面に水親和性のセラミック層を保有する型を用いて発泡ウレタン成形品を製造した。使用したウレタン原料は2液型のものであり、混合前のその組成は、重量%で次の通りであった。

A液

ポリオール	100重量部
触媒（33LV）	0.4重量部
シリコン系整泡剤	0.3重量部
ポリオール系架橋剤	1.5重量部
発泡剤（水）	3重量部

B液

TDIとポリメリックMDIの混合物

このA液とB液を100：50の割合で混合し、成形原料とした。

【0042】このウレタン原料を上記の型に注入し、70℃で2分間放置して、反応・硬化・発泡を行わせた。この状態では硬化は完全には完了していない。その後、蒸気分圧90%の水蒸気を含有する80℃の空気を流速0.5m/秒で5分間キャビティ内に吹き込んでから、直ちに成形品を脱型した。この時の離型は非常に容易であり、型のキャビティ面にはウレタン樹脂の付着は見られず、表面が滑らかで傷のない発泡ウレタン成形品が得られた。

【0043】同じ型を用いて同様に発泡ウレタン成形品の成形作業を50回反復実施したが、離型性は良好に保持され、高品質の発泡ウレタン成形品を効率よく製造することができた。

【0044】実施例2

脱型前に、40℃の5%エタノール水溶液を型に注入により導入した以外は、実施例1と同様に型の製作および成形作業を実施した。結果は実施例1と同様であった。

【0045】実施例3

セラミック形成用塗布液を次のようにして調製した。ア

ルミン酸ナトリウムの水溶液に塩酸を加えてpH5~10に調整することにより、 Al_2O_3 含有量50~200g/lのオール化したコロイド溶液を得た。このオール錯体含有コロイド溶液に、粒度1 μm 以下のアルミナ微粉末5~25g/lを添加し、セラミック形成用塗布液として使用した。

【0046】この塗布液を実施例1と同様に型のキャビティ面に塗布し、150℃で30分間焼付を行って、キャビティ面が厚さ1~2 μm のセラミック層で被覆された分割型を製作した。セラミック層中の水親和性構成成分を持つ化合物の含有量は定量しえないが、およそ表面積の40~50%はこのような化合物で占められるのではなかろうかと推測される。

【0047】この型を用いて実施例1および2と同様に発泡ウレタン成形品の成形作業を実施したところ、実施例1および2と同様に良好な離型性を保持して成形を反復実施することができた。

【0048】比較例1

実施例1と同様に型の製作および成形作業を実施したが、ただし、脱型前の水蒸気を含有する空気吹き込みを省略し、普通の大気中で80℃に10分間放置後直ちに脱型した。成形品の離型は不可能であった。

【0049】比較例2

実施例1で用いたのと同様のアルミニウム製の分割型を、セラミック層を形成せずに直接用いた以外は、実施例1と同様に成形作業を実施した。脱型前に実施例1と同様に水蒸気を含有する空気を吹き込んでから、脱型したところ、離型は困難であり、成形品の外観は材料破壊を呈していた。

【0050】比較例3

実施例1と同様に型の製作および成形作業を実施した。但し、脱型前の気体吹き込みは蒸気分圧5%の空気を用

いて行った。離型は全く不可能であり、成形品の外観は材料破壊を呈していた。

【0051】

【発明の効果】以上に詳述したように、本発明の方法により、キャビティ面にセラミック層が設けられた型を用いてウレタン成形原料を型に導入し、脱型前に水および/またはアルコールの含有気体または液体を型内に導入することにより、離型剤を塗布せずにウレタン成形品を型から容易に離型することが可能となる。

【0052】これにより、従来のウレタン成形品の成形作業では不可欠であった、各成形サイクル毎の多量の離型剤のキャビティ面への塗布が不要となる。その結果、この煩雑な成形サイクル毎の塗布作業がなくなって成形作業が簡略化される上、離型剤塗布に伴う各種の問題点、具体的には、離型剤による作業環境、型、さらには製品の離型剤による汚染がなくなり、また型に固着した離型剤を除去するための一定の成形サイクルごとの型の溶剤洗浄、多量の離型剤と溶剤の使用による経済的な損失、揮発性または有毒な溶剤を取り扱うことによる作業環境の悪化、型の洗浄により成形作業が中断することによる作業効率の低下、を避けることができる。

【0053】このように、本発明のウレタン成形品の製造方法は、ウレタン成形作業の環境を改善すると同時に、品質の良好な製品を低コストで効率よく製造することができ、工業的に実施した場合に優れた利点を発揮する方法である。

【図面の簡単な説明】

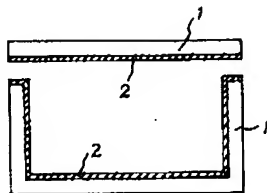
【図1】実施例で用いたウレタン成形用の分割型の略式断面図である。

【符号の説明】

1：型の本体

2：セラミック層

【図1】



フロントページの続き

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